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# Crystal structure of (*E*)-*N'*-[1-(4-aminophenyl)ethylidene]-2-hydroxy-5-iodobenzohydrazide methanol monosolvate

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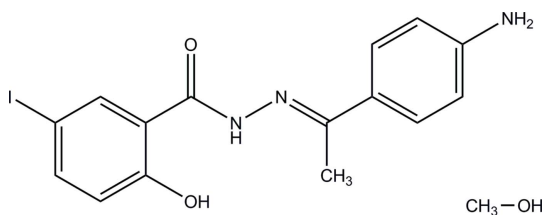
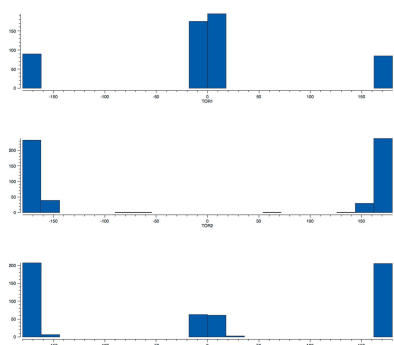
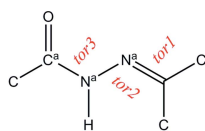
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In the title compound, C<sub>15</sub>H<sub>14</sub>IN<sub>3</sub>O<sub>2</sub>·CH<sub>3</sub>OH, two aromatic rings are linked by an *N*-substituted hydrazide function. The dihedral angle between the aromatic rings is 10.53 (8)°. The stereochemistry about the imine function is *E*. The methanol molecule forms an O—H···O hydrogen bond to the hydrazide O atom. In the crystal, chains of molecules running along the *c*-axis direction are formed by O—H···O hydrogen bonds. Adjacent chains are linked through N—H···O hydrogen bonds and  $\pi$ – $\pi$  stacking interactions. The intermolecular interactions in the crystal packing were investigated using Hirshfeld surface analysis, which indicated that the most significant contacts are H···H (38.2%), followed by C···H/H···C (20.6%), O···H/H···O (11.1%) and I···H/H···I (9.7%).

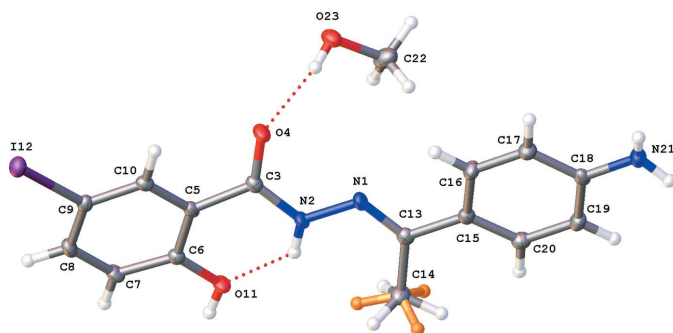
## 1. Chemical context

*N*-substituted hydrazides have been attracted much attention for their structures, coordination ability, biological activities and transformations to heterocyclic compounds (Majumdar *et al.*, 2014; Asif & Husain, 2013; Khan *et al.*, 2017). Derivatives of salicylic acid act as antibacterial (Kumar *et al.*, 2012; Cui *et al.*, 2014; Sarshira *et al.*, 2016), antifungal (Wodnicka *et al.*, 2017; Abbas *et al.*, 2017) and antitumor (Murty *et al.*, 2014) agents. In addition, some salicylhydrazones exhibit significant antitrypanosomal activity with IC<sub>50</sub> ranging from 1 to 34  $\mu$ M. *N*-substituted hydrazides containing the typical –C(O)–NH–N=C< functional group can be prepared by a condensation reaction between a hydrazide and a carbonyl compound (an aldehyde or a ketone).



As a continuation of our research work to synthesize derivatives of 5-iodosalicylhydrazide (Nguyen *et al.*, 2012), the new compound (*E*)-*N'*-[1-(4-aminophenyl)ethylidene]-2-hydroxy-5-iodobenzohydrazide methanol monosolvate was

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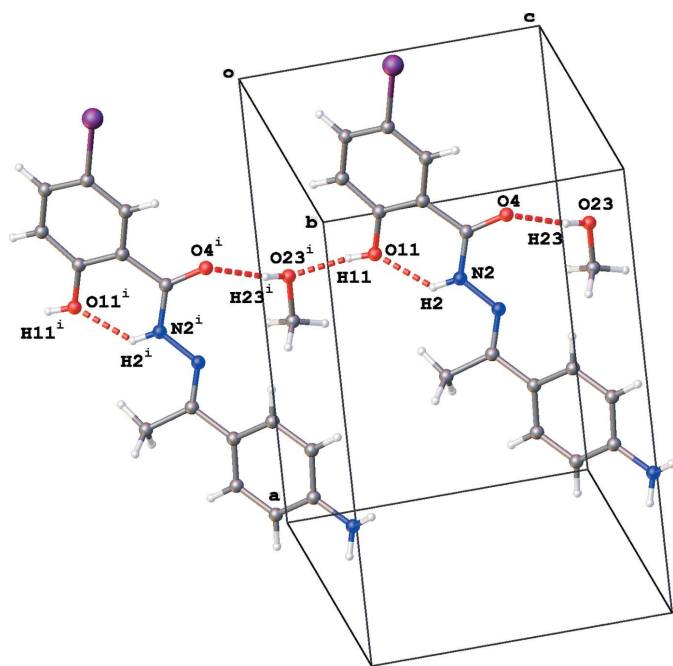


**Figure 1**  
View of the asymmetric unit of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii. Intra- and intermolecular hydrogen bonds are shown as dashed lines.

synthesized. The structure of the compound was determined by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and HR-MS spectroscopy as well as X-ray diffraction and the crystal structure is reported herein.

## 2. Structural commentary

The title compound (Fig. 1) crystallizes as a methanol monosolvate in the monoclinic space group  $P2_1/c$  with one hydrazide molecule and a methanol solvate molecule in the asymmetric unit. The OH group of methanol is hydrogen bonded to the hydrazide oxygen atom O4 (Fig. 1, Table 1). The dihedral angle between the aromatic rings is  $10.53(8)^\circ$ . This relatively planar character of the molecule is caused by an



**Figure 2**  
Part of the crystal packing of the title compound, showing the chain along the  $c$ -axis direction formed by  $\text{O}-\text{H}\cdots\text{O}$  hydrogen-bonding interactions [see Table 1; symmetry code: (i)  $x, y, z - 1$ ]. Only the major component of the disordered methyl group C14 is shown.

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ).

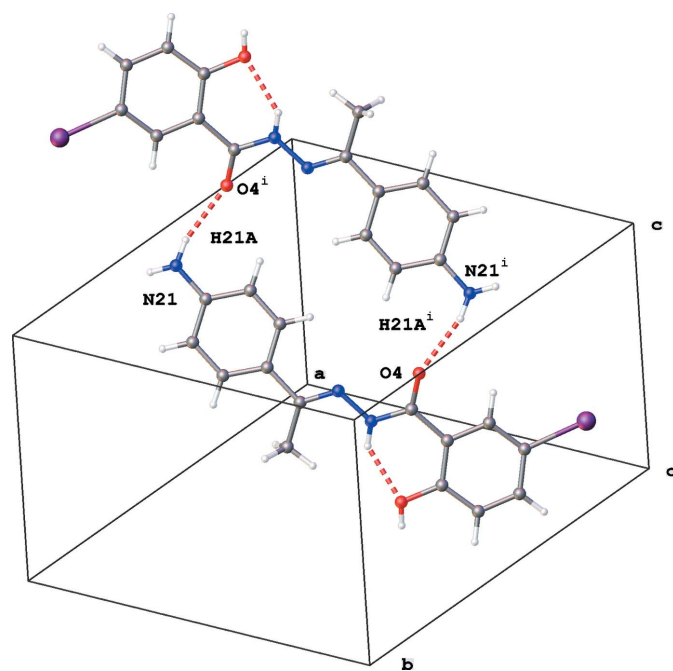
$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}23-\text{H}23\cdots\text{O}4$	0.80 (2)	1.97 (2)	2.7561 (18)	170 (3)
$\text{N}2-\text{H}2\cdots\text{O}11$	0.82 (3)	2.02 (2)	2.665 (2)	134.4 (19)
$\text{O}11-\text{H}11\cdots\text{O}23^i$	0.76 (3)	1.88 (3)	2.6323 (18)	172 (2)
$\text{N}21-\text{H}21\text{A}\cdots\text{O}4^{ii}$	0.85 (2)	2.14 (2)	2.961 (2)	164 (2)

Symmetry codes: (i)  $x, y, z - 1$ ; (ii)  $-x + 1, -y + 1, -z + 2$ .

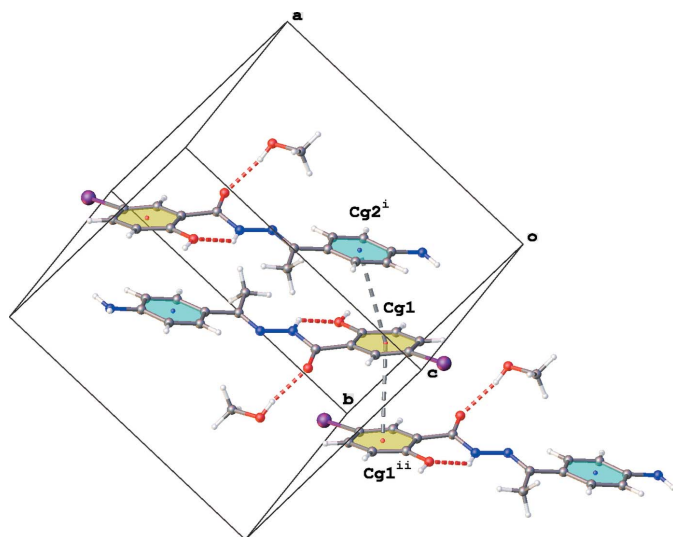
intramolecular hydrogen bond,  $\text{N}2-\text{H}2\cdots\text{O}11$  (Table 1), and the presence of the hydrazide functional group and the  $\text{C}13=\text{N}1$  double bond. The r.m.s. deviation from a plane through all 21 non-H atoms is  $0.291 \text{ \AA}$  [with a maximum deviation of  $0.838(1) \text{ \AA}$  observed for atom O4]. The torsion angles about the bonds of the hydrazide link between the two aromatic rings are:  $\text{C}15-\text{C}13=\text{N}1-\text{N}2 = -175.48(15)^\circ$ ,  $\text{C}13=\text{N}1-\text{N}2-\text{C}3 = 178.71(16)^\circ$  and  $\text{N}1-\text{N}2-\text{C}3-\text{C}5 = -172.18(15)^\circ$ . The stereochemistry about the imine function  $\text{C}13=\text{N}1$  is *E*. The planar character causes short contacts for the H atoms of methyl group C14 with the H atoms on atoms N2 and C20. As a consequence, this methyl group displays rotational disorder with occupancies of 0.66 (2) and 0.34 (2).

## 3. Supramolecular features

In the crystal, chains of molecules are formed along the  $c$ -axis direction by alternating  $\text{O}11-\text{H}11\cdots\text{O}23^i$  and  $\text{O}23-\text{H}23\cdots\text{O}4$  hydrogen bonds (Table 1 and Fig. 2). The interaction of adjacent chains through  $\text{N}21-\text{H}21\text{A}\cdots\text{O}4^{ii}$  hydrogen bonds results in the formation of dimers with graph set  $R_2^2(22)$  (Table 1 and Fig. 3). Both aromatic rings are

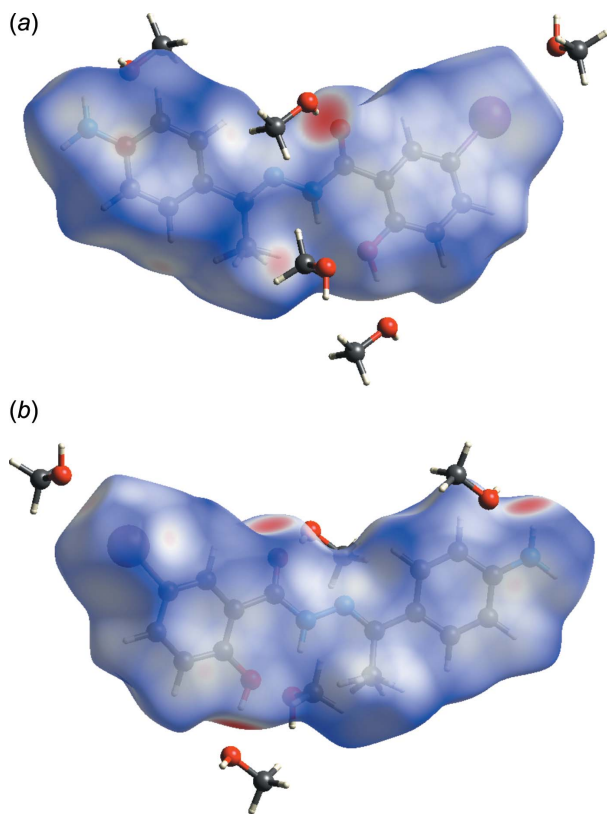


**Figure 3**  
Ring of graph-set motif  $R_2^2(22)$  formed by  $\text{N}-\text{H}\cdots\text{O}$  hydrogen-bonding interactions [see Table 1; symmetry code: (i)  $x - 1, y - 1, z - 2$ ].



**Figure 4**  
Part of the crystal packing of the title compound, showing the  $\pi$ - $\pi$  stacking interactions between the aminophenyl (blue) and iodophenyl (yellow) rings [symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x, -y + 1, -z + 1$ ].

involved in  $\pi$ - $\pi$  stacking interactions [ $Cg1 \cdots Cg1^i = 3.9769$  (10) Å, slippage 2.042 Å and  $Cg1 \cdots Cg2^{ii} = 3.8635$  (11) Å, slippage 1.596 Å;  $Cg1$  and  $Cg2$  are the centroids



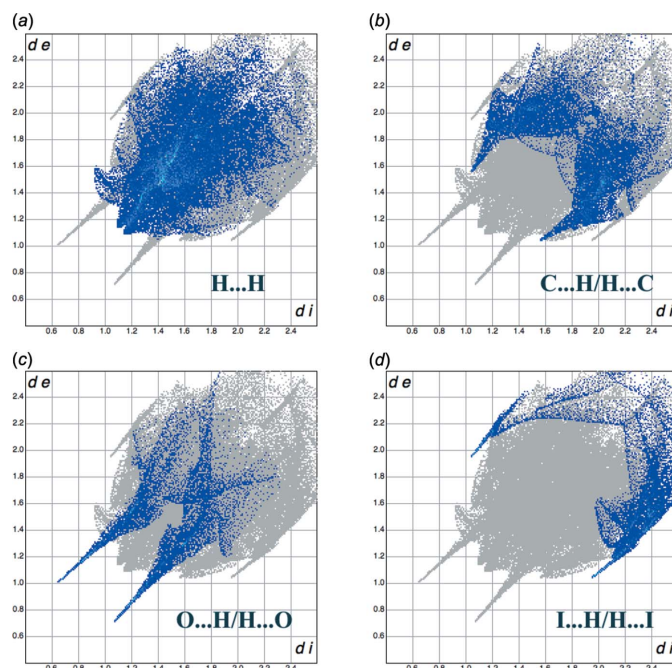
**Figure 5**  
Views of the Hirshfeld surface for the title compound mapped over  $d_{\text{norm}}$  over the range  $-0.740$  to  $1.296$  a.u. showing the closest methanol molecules.

of rings C5–C10 and C15–C20, respectively; Fig. 4]. The crystal packing contains no voids.

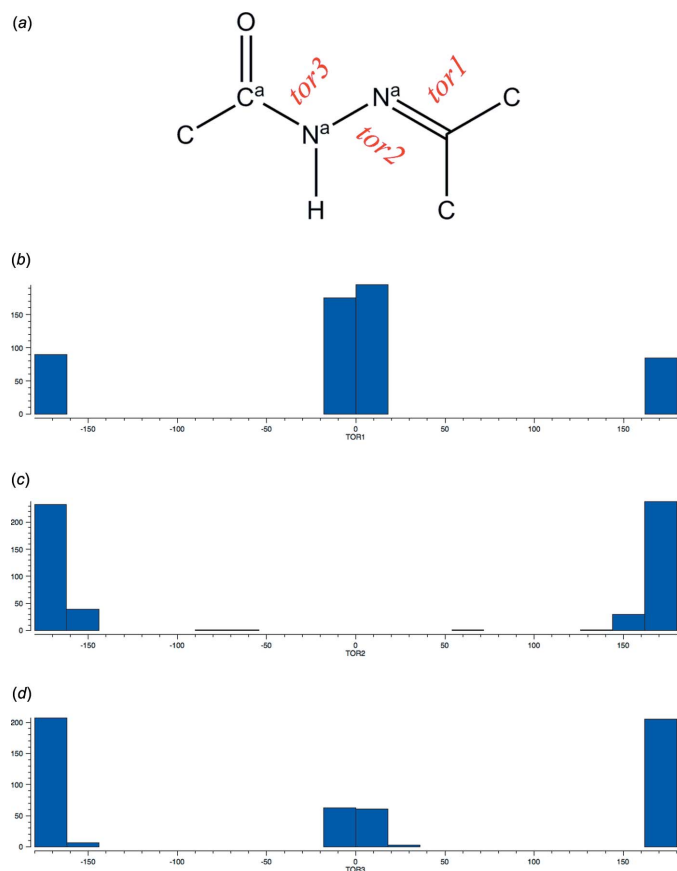
Additional insight into the crystal packing forces was obtained from a Hirshfeld surface analysis using *Crystal-Explorer* (McKinnon *et al.*, 2007; Spackman & Jayatilaka, 2009). The largest bright-red spots on the Hirshfeld surface mapped over  $d_{\text{norm}}$  correspond to the (N,O)–H $\cdots$ O hydrogen-bonding contacts (Fig. 5). The pale-red spots are the weaker C $\cdots$ H (C18 $\cdots$ H20), H $\cdots$ H (H14F $\cdots$ H22B), I $\cdots$ H (I12 $\cdots$ H21B) and I $\cdots$ O (I12 $\cdots$ O23) interactions. The most important 2D fingerprint plots, decomposed to highlight particular close contacts of atom pairs and their contribution, are given in Fig. 6. The relative contributions of the different intermolecular interactions to the Hirshfeld surface area in descending order are: H $\cdots$ H (38.2%), C $\cdots$ H/H $\cdots$ C (20.6%), O $\cdots$ H/H $\cdots$ O (11.1%), I $\cdots$ H/H $\cdots$ I (9.7%), N $\cdots$ H/H $\cdots$ N (7.2%) and C $\cdots$ C (5.7%). Contributions from the intermolecular non- or low-polar interactions are much greater than the contributions from the O $\cdots$ H contacts. The weak I $\cdots$ H interactions contribute significantly to the crystal packing.

#### 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.39, last update November 2017; Groom *et al.*, 2016)



**Figure 6**  
Two-dimensional fingerprint plots delineated into different contact types (a)–(d) for the title compound. Each blue dot represents a 0.01 Å bin of points on the Hirshfeld surface, with coordinates corresponding to distances (Å) from the points to the nearest interior ( $d_i$ ) and exterior ( $d_e$ ) nuclei. Increasing intensity of overlapping points is shown by a colour coding from blue to cyan. The grey background contours correspond to the plot integrated for all contact types.



**Figure 7**  
(a) The *N*-substituted hydrazide fragment used for a search in the CSD (*a* refers to acyclic). (b)–(d) Histograms of torsion angles *tor1*, *tor2* and *tor3*, respectively.

for the central *N*-substituted hydrazide moiety (Fig. 7a) resulted in 461 hits. The histograms of the torsion angles show the distribution for torsion angles *tor1* (Fig. 7b) and *tor3* (Fig. 7d) as expected for a planar conjugated system. However, the histogram of torsion angle *tor2* (Fig. 7c) shows the presence of three non-planar entries with torsion angle values of  $-72.1$  (refcode XIJTAN; Buzykin *et al.*, 2012),  $-67.9$  (refcode NIZTUM; Muniz-Miranda *et al.*, 2008) and  $+68.6^\circ$  (XIJTAN; Buzykin *et al.*, 2012).

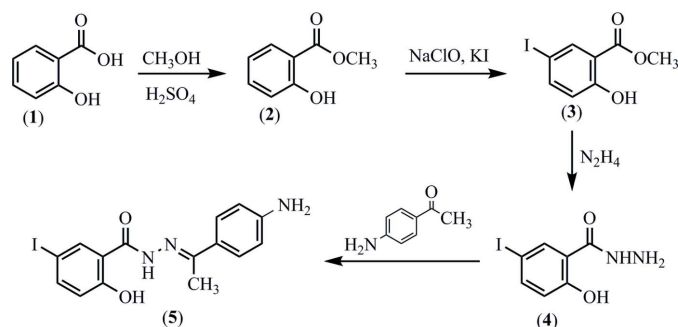
## 5. Synthesis and crystallization

The reaction scheme used to synthesize the title compound, **5**, is shown in Fig. 8. Methyl salicylate, methyl 2-hydroxy-5-iodobenzoate and 2-hydroxy-5-iodobenzohydrazide were prepared from salicylic acid according to the method described in our earlier work (Nguyen *et al.*, 2012).

Methyl salicylate, **2**: liquid; b.p. 494–495 K, yield 73%.

Methyl 2-hydroxy-5-iodobenzoate (methyl 5-iodosalicylate), **3**: white needles, m.p. 347–348 K, yield 85%; IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3156, 3080, 2949, 1676, 1604, 527.

2-Hydroxy-5-iodobenzohydrazide, **4**: white needles, m.p. 451 K, yield 79%; IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3405, 3322, 1626, 1574, 529;  $^1\text{H}$  NMR ( $\delta$ , ppm): 12.41 (1H, *br*, OH), 10.12 (1H, *br*, NH), 8.12



**Figure 8**  
Reaction scheme for the title compound.

(1H, *d*,  $^4J = 2.0$ , ArH), 7.65 (1H, *dd*,  $^3J = 9.0$  Hz,  $^4J = 2.0$  Hz, ArH), 6.75 (1H, *d*,  $^3J = 9.0$  Hz, ArH), 4.80 (2H, *br*, NH<sub>2</sub>);  $^{13}\text{C}$  NMR: 166.1 (CO), 158.9, 141.3, 135.5, 119.9, 117.4, 80.5.

(*E*)-*N*'-[1-(4-aminophenyl)ethylidene]-2-hydroxy-5-iodobenzohydrazide, **5**: A solution of 2-hydroxy-5-iodobenzohydrazide **4** and 4'-aminoacetophenone was refluxed for 2 h. The reaction mixture was cooled down to room temperature and the precipitate obtained was filtered off and crystallized from methanol to give **5** as yellow crystals in 78% yield. M.p. 515–516 K. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3440, 3298, 3201 (OH, N–H), 2932 (*Csp*<sup>3</sup>–H), 1634, 1577 (C=O, C=N);  $^1\text{H}$  NMR ( $\delta$ , ppm and *J*, Hz): 11.11 (1H, *s*, NH), 8.23 (1H, *s*, ArH), 7.70

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>15</sub> H <sub>14</sub> IN <sub>3</sub> O <sub>2</sub> ·CH <sub>4</sub> O
<i>M<sub>r</sub></i>	427.23
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.9877 (10), 14.8982 (10), 8.5593 (6)
$\beta$ (°)	91.806 (2)
<i>V</i> (Å <sup>3</sup> )	1655.3 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.95
Crystal size (mm)	0.41 × 0.27 × 0.22
Data collection	
Diffractometer	Bruker D8 Quest CMOS
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2014)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.613, 0.746
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	45415, 3394, 3086
<i>R<sub>int</sub></i>	0.044
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.625
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.017, 0.041, 1.06
No. of reflections	3394
No. of parameters	231
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.61, $-0.24$

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

(1H, *d*,  $^3J = 8.5$ , ArH), 7.59 (2H, *d*,  $^3J = 8.5$ , ArH), 6.86 (1H, *d*,  $^3J = 8.5$ , ArH), 6.59 (2H, *d*,  $^3J = 8.5$ , ArH), 5.55 (2H, *br*, NH<sub>2</sub>), 2.22 (3H, *s*, -CH<sub>3</sub>); <sup>13</sup>C NMR ( $\delta$ , ppm): 161.1 (C=O), 157.0, 154.8, 150.9, 141.6, 138.7, 128.3, 125.2, 121.0, 120.1, 113.7, 82.0, 14.1; MS: *m/z* 396.0069 (*M*+H)<sup>+</sup>, calculated for C<sub>15</sub>H<sub>15</sub>IN<sub>3</sub>O<sub>2</sub>: 396.0209.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms attached to atoms N2, N21, O11 and O23 were found in a difference-Fourier map and refined freely. The other H atoms were placed at calculated positions and refined in riding mode, with C–H distances of 0.95 (aromatic) and 0.98 Å (CH<sub>3</sub>), and isotropic displacement parameters equal to 1.2 $U_{eq}$  of the parent atoms (1.5 $U_{eq}$  for CH<sub>3</sub>). The difference-Fourier map indicated disorder for the H atoms of methyl group C14. The final occupancy factors for the two sets of H atoms are 0.66 (2) and 0.34 (2). In the final cycles of refinement, two reflections showing very poor agreement were omitted as outliers.

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## supporting information

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## Crystal structure of (*E*)-*N'*-[1-(4-aminophenyl)ethylidene]-2-hydroxy-5-iodobenzohydrazide methanol monosolvate

Cong Nguyen Tien, Huong Le Thi Thu, Thin Nguyen Van, Trung Vu Quoc, Manh Vu Quoc, Thang Pham Chien and Luc Van Meervelt

### Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2013); data reduction: *SAINTE* (Bruker, 2013); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### (*E*)-*N'*-[1-(4-Aminophenyl)ethylidene]-2-hydroxy-5-iodobenzohydrazide methanol monosolvate

#### Crystal data

$C_{15}H_{14}IN_3O_2 \cdot CH_4O$

$M_r = 427.23$

Monoclinic,  $P2_1/c$

$a = 12.9877$  (10) Å

$b = 14.8982$  (10) Å

$c = 8.5593$  (6) Å

$\beta = 91.806$  (2)°

$V = 1655.3$  (2) Å<sup>3</sup>

$Z = 4$

$F(000) = 848$

$D_x = 1.714$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9842 reflections

$\theta = 3.1\text{--}30.5^\circ$

$\mu = 1.95$  mm<sup>-1</sup>

$T = 100$  K

Block, yellow

$0.41 \times 0.27 \times 0.22$  mm

#### Data collection

Bruker D8 Quest CMOS  
diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2014)

$T_{\min} = 0.613$ ,  $T_{\max} = 0.746$

45415 measured reflections

3394 independent reflections

3086 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 26.4^\circ$ ,  $\theta_{\min} = 3.1^\circ$

$h = -16 \rightarrow 16$

$k = -18 \rightarrow 18$

$l = -10 \rightarrow 10$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.017$

$wR(F^2) = 0.041$

$S = 1.06$

3394 reflections

231 parameters

1 restraint

Primary atom site location: structure-invariant  
direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0145P)^2 + 1.4435P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.61 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.40946 (11)	0.57600 (10)	0.63743 (17)	0.0163 (3)	
N2	0.33272 (11)	0.55807 (10)	0.52645 (18)	0.0161 (3)	
H2	0.3379 (16)	0.5699 (15)	0.433 (3)	0.023 (6)*	
C3	0.24587 (13)	0.51777 (11)	0.5728 (2)	0.0148 (3)	
O4	0.22915 (10)	0.50292 (9)	0.71249 (14)	0.0199 (3)	
C5	0.17050 (13)	0.48847 (12)	0.4474 (2)	0.0140 (3)	
C6	0.16570 (13)	0.52242 (11)	0.2943 (2)	0.0145 (3)	
C7	0.08776 (14)	0.49318 (12)	0.1909 (2)	0.0170 (4)	
H7	0.081025	0.519641	0.090110	0.020*	
C8	0.01991 (14)	0.42619 (12)	0.2326 (2)	0.0172 (4)	
H8	-0.031928	0.405794	0.160228	0.021*	
C9	0.02861 (13)	0.38912 (12)	0.3817 (2)	0.0150 (3)	
C10	0.10096 (13)	0.42151 (12)	0.48894 (19)	0.0147 (3)	
H10	0.103575	0.398069	0.592210	0.018*	
O11	0.23620 (10)	0.58419 (9)	0.25082 (15)	0.0182 (3)	
H11	0.233 (2)	0.5920 (18)	0.163 (3)	0.042 (8)*	
I12	-0.06829 (2)	0.28322 (2)	0.44470 (2)	0.01876 (5)	
C13	0.49324 (13)	0.61305 (12)	0.5921 (2)	0.0151 (3)	
C14	0.51380 (15)	0.64301 (14)	0.4276 (2)	0.0217 (4)	
H14A	0.454135	0.628694	0.359179	0.033*	0.66 (2)
H14B	0.574751	0.611872	0.390192	0.033*	0.66 (2)
H14C	0.525871	0.707940	0.426604	0.033*	0.66 (2)
H14D	0.506928	0.591666	0.356473	0.033*	0.34 (2)
H14E	0.583785	0.667320	0.423635	0.033*	0.34 (2)
H14F	0.464045	0.689520	0.395866	0.033*	0.34 (2)
C15	0.57516 (13)	0.62386 (12)	0.7151 (2)	0.0151 (3)	
C16	0.56846 (14)	0.57802 (13)	0.8582 (2)	0.0187 (4)	
H16	0.510394	0.540934	0.875386	0.022*	
C17	0.64415 (14)	0.58565 (12)	0.9740 (2)	0.0183 (4)	
H17	0.637198	0.554354	1.069845	0.022*	
C18	0.73134 (13)	0.63918 (12)	0.9518 (2)	0.0156 (3)	
C19	0.73773 (14)	0.68645 (12)	0.8117 (2)	0.0176 (4)	
H19	0.795006	0.724630	0.795497	0.021*	
C20	0.66115 (14)	0.67820 (12)	0.6957 (2)	0.0175 (4)	
H20	0.667530	0.710410	0.600736	0.021*	
N21	0.80719 (13)	0.64660 (12)	1.06816 (19)	0.0195 (3)	
H21A	0.8080 (17)	0.6075 (16)	1.140 (3)	0.025 (6)*	
H21B	0.8644 (19)	0.6701 (16)	1.040 (3)	0.028 (6)*	

C22	0.31350 (17)	0.69396 (14)	0.9344 (3)	0.0285 (5)
H22A	0.294430	0.732318	0.845110	0.043*
H22B	0.380013	0.665329	0.916393	0.043*
H22C	0.318802	0.730503	1.029528	0.043*
O23	0.23658 (11)	0.62647 (9)	0.95224 (15)	0.0213 (3)
H23	0.242 (2)	0.5898 (15)	0.885 (3)	0.040 (8)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0147 (7)	0.0195 (8)	0.0143 (7)	−0.0010 (6)	−0.0037 (6)	−0.0009 (6)
N2	0.0166 (8)	0.0217 (8)	0.0096 (7)	−0.0024 (6)	−0.0033 (6)	0.0005 (6)
C3	0.0170 (9)	0.0125 (8)	0.0147 (8)	0.0020 (7)	−0.0012 (7)	−0.0008 (7)
O4	0.0229 (7)	0.0257 (7)	0.0109 (6)	−0.0068 (5)	−0.0023 (5)	0.0014 (5)
C5	0.0140 (8)	0.0150 (8)	0.0128 (8)	0.0023 (7)	−0.0015 (6)	−0.0025 (7)
C6	0.0163 (8)	0.0131 (8)	0.0142 (8)	0.0010 (7)	0.0009 (7)	−0.0009 (7)
C7	0.0216 (9)	0.0175 (9)	0.0117 (8)	0.0021 (7)	−0.0031 (7)	0.0013 (7)
C8	0.0166 (9)	0.0193 (9)	0.0154 (8)	0.0010 (7)	−0.0048 (7)	−0.0025 (7)
C9	0.0135 (8)	0.0141 (8)	0.0175 (9)	0.0002 (7)	0.0009 (7)	−0.0018 (7)
C10	0.0166 (8)	0.0155 (9)	0.0118 (8)	0.0031 (7)	−0.0001 (7)	0.0004 (7)
O11	0.0225 (7)	0.0215 (7)	0.0104 (6)	−0.0055 (5)	−0.0012 (5)	0.0029 (5)
I12	0.01767 (7)	0.01657 (7)	0.02193 (7)	−0.00289 (4)	−0.00078 (4)	0.00057 (5)
C13	0.0166 (9)	0.0131 (8)	0.0155 (8)	0.0020 (7)	0.0000 (7)	−0.0006 (7)
C14	0.0206 (9)	0.0279 (10)	0.0166 (9)	−0.0017 (8)	−0.0009 (7)	0.0053 (8)
C15	0.0143 (8)	0.0154 (8)	0.0155 (8)	0.0018 (7)	0.0000 (7)	−0.0009 (7)
C16	0.0154 (9)	0.0216 (9)	0.0190 (9)	−0.0051 (7)	0.0002 (7)	0.0021 (7)
C17	0.0180 (9)	0.0210 (9)	0.0160 (8)	−0.0022 (7)	0.0009 (7)	0.0026 (7)
C18	0.0149 (8)	0.0157 (9)	0.0162 (8)	0.0027 (7)	−0.0006 (7)	−0.0050 (7)
C19	0.0150 (9)	0.0169 (9)	0.0210 (9)	−0.0027 (7)	0.0012 (7)	0.0005 (7)
C20	0.0187 (9)	0.0172 (9)	0.0168 (9)	0.0007 (7)	0.0022 (7)	0.0017 (7)
N21	0.0170 (8)	0.0230 (9)	0.0182 (8)	−0.0038 (7)	−0.0019 (6)	0.0006 (7)
C22	0.0291 (11)	0.0251 (10)	0.0318 (11)	−0.0050 (9)	0.0107 (9)	−0.0034 (9)
O23	0.0277 (7)	0.0223 (7)	0.0140 (6)	−0.0043 (6)	0.0014 (5)	−0.0005 (6)

*Geometric parameters (Å, °)*

N1—N2	1.381 (2)	C14—H14C	0.9800
N1—C13	1.291 (2)	C14—H14D	0.9800
N2—H2	0.82 (2)	C14—H14E	0.9800
N2—C3	1.349 (2)	C14—H14F	0.9800
C3—O4	1.242 (2)	C15—C16	1.407 (2)
C3—C5	1.495 (2)	C15—C20	1.394 (3)
C5—C6	1.404 (2)	C16—H16	0.9500
C5—C10	1.399 (2)	C16—C17	1.379 (3)
C6—C7	1.394 (2)	C17—H17	0.9500
C6—O11	1.359 (2)	C17—C18	1.403 (3)
C7—H7	0.9500	C18—C19	1.396 (3)
C7—C8	1.386 (3)	C18—N21	1.383 (2)



C8—H8	0.9500	C19—H19	0.9500
C8—C9	1.392 (2)	C19—C20	1.388 (3)
C9—C10	1.380 (2)	C20—H20	0.9500
C9—I12	2.0993 (17)	N21—H21A	0.85 (2)
C10—H10	0.9500	N21—H21B	0.86 (2)
O11—H11	0.76 (3)	C22—H22A	0.9800
C13—C14	1.509 (2)	C22—H22B	0.9800
C13—C15	1.482 (2)	C22—H22C	0.9800
C14—H14A	0.9800	C22—O23	1.429 (2)
C14—H14B	0.9800	O23—H23	0.800 (16)
C13—N1—N2	118.21 (15)	C13—C14—H14A	109.5
N1—N2—H2	123.2 (15)	C13—C14—H14B	109.5
C3—N2—N1	118.42 (15)	C13—C14—H14C	109.5
C3—N2—H2	118.4 (15)	C13—C14—H14D	109.5
N2—C3—C5	116.98 (15)	C13—C14—H14E	109.5
O4—C3—N2	122.40 (16)	C13—C14—H14F	109.5
O4—C3—C5	120.59 (16)	C16—C15—C13	120.20 (16)
C6—C5—C3	125.00 (16)	C20—C15—C13	122.59 (16)
C10—C5—C3	116.05 (15)	C20—C15—C16	117.21 (16)
C10—C5—C6	118.94 (16)	C15—C16—H16	119.2
H14Aa—C14—H14B	109.5	C17—C16—C15	121.57 (17)
H14Ba—C14—H14C	109.5	C17—C16—H16	119.2
H14Aa—C14—H14C	109.5	C16—C17—H17	119.7
H14Db—C14—H14E	109.5	C16—C17—C18	120.63 (17)
H14Eb—C14—H14F	109.5	C18—C17—H17	119.7
H14Db—C14—H14F	109.5	C19—C18—C17	118.27 (16)
C7—C6—C5	119.36 (16)	N21—C18—C17	120.49 (17)
O11—C6—C5	119.30 (15)	N21—C18—C19	121.22 (17)
O11—C6—C7	121.33 (16)	C18—C19—H19	119.7
C6—C7—H7	119.4	C20—C19—C18	120.60 (17)
C8—C7—C6	121.12 (16)	C20—C19—H19	119.7
C8—C7—H7	119.4	C15—C20—H20	119.2
C7—C8—H8	120.4	C19—C20—C15	121.68 (17)
C7—C8—C9	119.19 (16)	C19—C20—H20	119.2
C9—C8—H8	120.4	C18—N21—H21A	117.5 (16)
C8—C9—I12	120.11 (13)	C18—N21—H21B	115.7 (15)
C10—C9—C8	120.35 (16)	H21A—N21—H21B	119 (2)
C10—C9—I12	119.54 (13)	H22A—C22—H22B	109.5
C5—C10—H10	119.6	H22A—C22—H22C	109.5
C9—C10—C5	120.78 (16)	H22B—C22—H22C	109.5
C9—C10—H10	119.6	O23—C22—H22A	109.5
C6—O11—H11	111 (2)	O23—C22—H22B	109.5
N1—C13—C14	125.66 (16)	O23—C22—H22C	109.5
N1—C13—C15	115.19 (15)	C22—O23—H23	109.2 (19)
C15—C13—C14	119.13 (15)		
N1—N2—C3—O4	5.9 (3)	C8—C9—C10—C5	-3.6 (3)

N1—N2—C3—C5	-172.18 (15)	C10—C5—C6—C7	4.3 (3)
N1—C13—C15—C16	13.9 (2)	C10—C5—C6—O11	-176.74 (15)
N1—C13—C15—C20	-166.49 (17)	O11—C6—C7—C8	175.98 (16)
N2—N1—C13—C14	3.0 (3)	I12—C9—C10—C5	176.29 (13)
N2—N1—C13—C15	-175.48 (15)	C13—N1—N2—C3	178.71 (16)
N2—C3—C5—C6	-20.8 (3)	C13—C15—C16—C17	179.02 (17)
N2—C3—C5—C10	158.64 (16)	C13—C15—C20—C19	-179.11 (17)
C3—C5—C6—C7	-176.25 (16)	C14—C13—C15—C16	-164.75 (17)
C3—C5—C6—O11	2.7 (3)	C14—C13—C15—C20	14.9 (3)
C3—C5—C10—C9	-179.52 (15)	C15—C16—C17—C18	-0.6 (3)
O4—C3—C5—C6	161.03 (17)	C16—C15—C20—C19	0.6 (3)
O4—C3—C5—C10	-19.5 (2)	C16—C17—C18—C19	1.9 (3)
C5—C6—C7—C8	-5.1 (3)	C16—C17—C18—N21	-179.92 (17)
C6—C5—C10—C9	0.0 (3)	C17—C18—C19—C20	-2.0 (3)
C6—C7—C8—C9	1.5 (3)	C18—C19—C20—C15	0.8 (3)
C7—C8—C9—C10	2.9 (3)	C20—C15—C16—C17	-0.6 (3)
C7—C8—C9—I12	-177.01 (13)	N21—C18—C19—C20	179.84 (17)

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O23—H23 $\cdots$ O4	0.80 (2)	1.97 (2)	2.7561 (18)	170 (3)
N2—H2 $\cdots$ O11	0.82 (3)	2.02 (2)	2.665 (2)	134.4 (19)
O11—H11 $\cdots$ O23 <sup>i</sup>	0.76 (3)	1.88 (3)	2.6323 (18)	172 (2)
N21—H21A $\cdots$ O4 <sup>ii</sup>	0.85 (2)	2.14 (2)	2.961 (2)	164 (2)

Symmetry codes: (i)  $x, y, z-1$ ; (ii)  $-x+1, -y+1, -z+2$ .